

Low Cost CuS₂ Thin Film by Non-Vacuum Techniques

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Abstract: The opto-electronic properties of copper sulphide can be tuned by the controlled incorporation of selenium. In this paper we report the growth of Copper Sulpho Selenide (CuS₂) using a hybrid process involving the Chemical Bath Deposition (CBD) of CuS and Electrodeposition (ED) of selenium precursors on CuS. The incorporation of selenium affects the structural, optical and morphological properties of the resulting film, which are characterized by X-ray diffraction (XRD), UV-VIS Spectrometer and Scanning Electron Microscopy (SEM) & Atomic Force Microscopy (AFM). It is found that the incorporation of selenium resulted better crystalline structure and excellent optical properties. The SEM pictures confirm the uniform surface morphology with good distribution of crystallites. This new approach encompasses many advantages over the conventional methods in terms of reaction conditions (i.e. lower temperature), product quality, and cost. CuS₂ thin film obtained by this method could be potential building blocks to construct functional devices, solar cell, etc.

Keywords: Thin Films, surface properties, EDAX, Optical Properties, Electrochemical Techniques.

1 Introduction

Chalcopyrite semiconductor thin films viz. CIGS, CZTS and CIS are powerful candidates for absorbing layer in solar cells, as they have many advantages like simple structure, low cost substrate, compatibility, tuneable optical band gap and efficiency up to 25% [1-3]. CIGS thin films are commonly prepared by vacuum techniques such as sputtering [4], molecular beam deposition [5] etc. In the above mentioned preparation methods, the precursors were sputtered without Se and then it is annealed in the presence of Se [6]. It has been reported elsewhere, that an improvement in the properties of a Photo Voltaic (PV) cell are observed by the incorporation of S with Se. Variation in the ratio of sulfur to selenium also reflected in structural, electrical and optical properties of the thin film. Hence, these absorbers gain considerable attention in the fabrication of thin film solar cell [7].

Copper based chalcopyrite Cu(In,Ga)(Se,S)₂ (CIGSSe) as an absorbing material has been extensively investigated for the fabrication of thin film solar cell [8]. The adjustable direct band gap and high absorption coefficient make this chalcopyrite as an ideal material for thin film in PV cells. At the laboratory scale, conversion efficiencies of these fabricated cells is around 19%. To prepare the above said thin film, selenization process is adopted because it develops single phase absorbers for solar cells. Even though the selenisation process for alloys were carried out using H₂Se in Ar atmosphere, due to toxicity, volatility, volume expansion and reactivity of H₂Se led to reluctance

in adopting this route. A number of deposition methods have been investigated to fabricate thin film solar cells viz., vacuum based techniques like RF and DC sputtering [9,10], chemical vapour deposition [11], thermal evaporation [12], molecular beam epitaxy [5] etc, and non-vacuum techniques such as electro deposition [13], spray pyrolysis [14], spin coating [15], chemical bath deposition [16] and paste method [17]. Among these, many researchers have optimistic way that sputtering method is best for the preparation of thin film. Although vacuum based deposition techniques have produced high efficiency devices in the laboratory scale, the large scale operation of some of these techniques are limited due to scale-up challenges and high expenditure. These techniques require more intensive energy than non vacuum techniques, because it requires high energy for evaporating the materials onto heated substrates.

Therefore, it is highly desirable to develop an environmental friendly, easily scalable and relatively safe process for the fabrication of high-quality thin films. In this context, for the first time two environmental friendly non vacuum techniques are used to develop a CuS₂ thin film for solar cells. The main aim of this research work is to adopt simple, cost effective non-vacuum selenization process to get highly desirable thin film for PV cells. Fabrication of CuS₂ thin film was carried out in two steps, in the first step copper sulphide (CuS) thin film was developed by CBD technique and in second step

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selenization was carried out by ED, which involves the exposure of a metallic precursor to a reactive selenium environment to produce the desired selenide compound. The characterization of the fabricated thin film was carried out for its optical, surface and structural properties.

2 Experimental

The CuS₂ film was prepared at room temperature on ITO coated glass substrate. In the first step, the thin film of CuS was deposited by CBD technique. Aqueous solution of copper sulphate (0.1M), thiourea and triethanolamine were prepared separately using double distilled water before the experiment. The copper sulphate solution was taken in a beaker, other precursors such as triethanolamine (2.5 ml), 1M thiourea (5ml) and 30% ammonia solution (5ml) were added slowly one after the other with constant stirring. The bath solution was diluted to 50 ml using double distilled water [16].

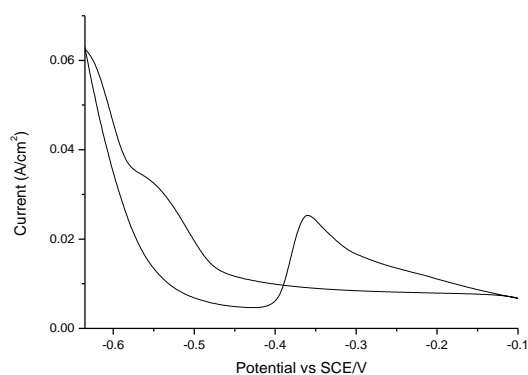


Fig.1. Cyclic Voltammogram of selenization on CuS thin film.

The triethanolamine serves as a complexing agent to chelate with copper ions. The deposition of CuS films is based on the slow release of Cu²⁺ and S²⁻ ions in the solution, which are then condensed on the glass substrates [18].

The thiourea and ammonia solution used as a source for sulphide ions and to maintain the pH of the bath at 11 respectively. In the second step, the deposited CuS thin film was subjected to selenisation process using the CH Electrochemical Analyzer(660D) with a three-electrode system, consisting of the CuS/ITO thin film as working electrode, a pure platinum rod as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The Cyclic Voltametric (CV) technique was adopted for the selenization using 0.1M aqueous solution of selenous acid (H₂SeO₃ Aldrich). The temperature of the electrolyte was maintained at 25°C and the Selenisation was carried out by applying the voltage between -0.7V to -0.1V vs. SCE for 20 min at room temperature. In order to get better homogenization equi molar ratio of S and Se was

maintained [18]. The cyclic voltammogram obtained during the process is as shown in Fig-1. After the ED film was rinsed thoroughly with distilled water and then dried.

3 Results and Discussion

The structural analysis of the thin film was carried out using XRD (Bruker D2 phaser) with CuK α radiation (30kV and 40mA) with $\lambda = 1.54056 \text{ \AA}$ for 2θ values over 20–90°. The surface morphology and topography was carried out by using Atomic Force Microscopy (AFM), Park System in non contact mode with Silicon Nitride tip and Scanning Electron Microscopy (SEM: Phenom S340N) respectively. Optical absorption data such as absorbance (A), transmittance (T) and reflectance (R) were obtained with a Shimadzu UV-1800, spectrophotometer at normal incidence of light in the wavelength range of 300-1100 nm.

3.1 Structural Characterization

XRD is a powerful non-destructive method for characterization by which the crystal structure, grain size and orientation factor can be determined.

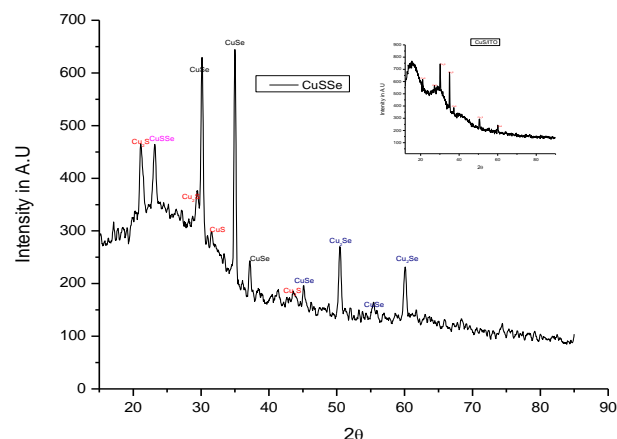


Fig.2. XRD image of CuS₂ on ITO substrate (the inset is for CuS thin film)

The typical XRD patterns obtained before and after selenisation of the thin film are shown in Fig.2, where the major peaks of CuS₂ are identified and labelled. It can be seen from Fig. 2 the diffraction peaks of CuS₂ thin film follow the standard bulk crystal structure patterns of CuS, CuSe and their different phases. However, the XRD pattern of CuS₂ film shows the characteristic peak of Cu(S,Se) phases, and the peaks corresponding to secondary phases of such as Cu₂S, CuS, CuSe and CuSe₂. These phases were identified using the Diffraction eva software and are exactly matching with the library files for CuSe- COD: 9000063, CuSe₂ – COD: 9009853, Cu₂S-COD: 9008297 and CuS-COD: 1010955. In addition, the patterns of XRD show the diffraction peaks of the films shift systematically to the left

due to the increase in lattice parameter with Se replacing S in the CuS matrix [19].

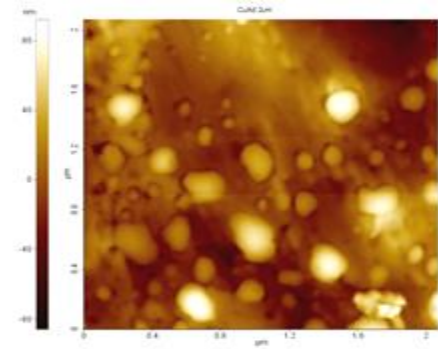
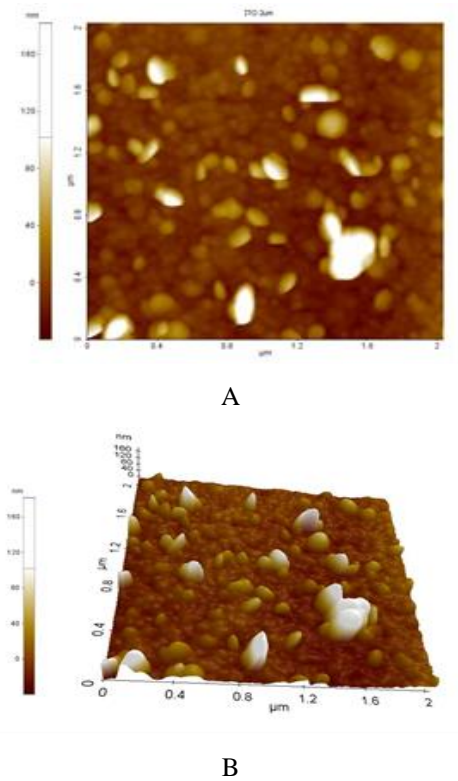
$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

The average grain size (D) is calculated using the Scherrer's formula (c.f. Eq.1) from the full-width at half maximum (FWHM), β corresponding peak of the XRD pattern [20]. The calculated average grain size using observed peaks for as-deposited copper sulfo selenide and CuS thin film is about 22 nm and 28 nm respectively.

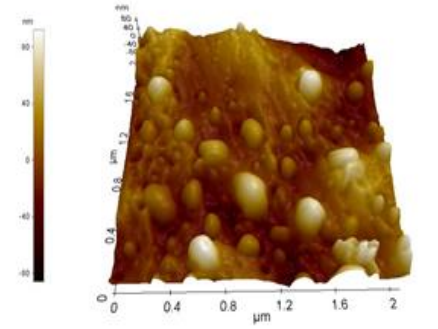
3.2 Surface morphology

3.2.1 Atomic Force Microscopy (AFM)

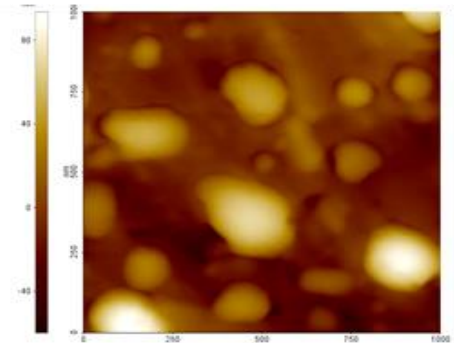
AFM was used to study the surface morphologies of the thin film fabricated on the ITO-coated glass substrate. It gives the information on structure and surface roughness of the thin films. This technique is capable of mapping three-dimensional images of the surface. The surface morphology of CuS thin film is shown in the Fig. 3(A, B). AFM images revealed that the prepared thin film is of granular without any agglomeration. The Root Mean Square (RMS) value calculated from different areas of the film indicates the surface roughness of the film which is 29.8nm. The standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness [21].



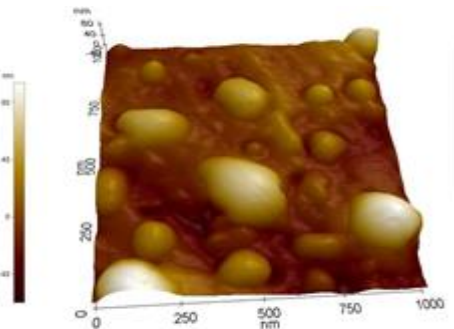
C



D



E

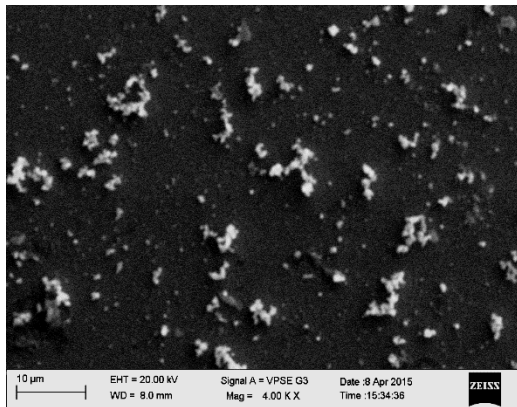


F

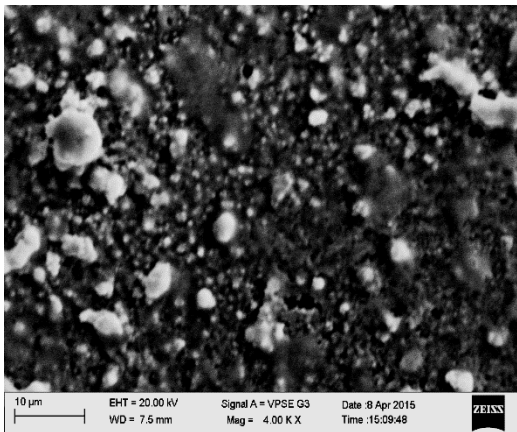
Fig. 3 AFM images of CuS (A, B) and CuSSe (C to F)

The surface morphology after selenizations are shown in the Fig.3(C-F). Selenium particles are distributed almost uniformly throughout the substrate, but there is an agglomeration of particles in most of the cases as evident from the 2D micrographs. RMS roughness decreases from an initial value of 29.8nm to 14.81nm for the as-grown CuS film after the selenization. Despite the roughness, it is clear from the AFM images that the film morphologies for CuS and CuS_{Se} are quite different.

3.2.2 Scanning Electron Microscopy (SEM)



A



B

Fig.4. SEM micrograph of CuS (A) and CuS_{Se} (B) on ITO glass substrate.

The Fig.4(A, B) are the Scanning Electron Micrographs (SEM) obtained for CuS and CuS_{Se} thin films respectively, deposited at room temperature. The observed morphology is very much different before and after selenization. The thin film of CuS (cf. Fig.4A) is uniform, smooth, homogeneous without any visible pores or cracks and covers the entire surface of the substrate. After selenization of CuS film Selenium is distributed almost uniformly as shown in (Fig.4B). From the micrograph, it is clear that the particles are crystalline in nature they are closely packed without agglomeration and cracks. The increase in grain size with increase in annealing temperatures is a common

observation in thin film phenomenon. The surface of copper selenide has smoother contour with some edge lines between the grains of large size. It is seen that there is overlapping of large number of small spherical grains which are aggregated together to form relatively big grain size. This type of surface is related to formation of limited initial nucleons at specific places of the substrate and then grow with new nucleons till the critical size reached [22]. The incorporated selenium particle helps in diffraction of light and avoids the reflection. This enhances the absorption of sun light, which is also reflected in UV-VIS spectra, intern may increases the efficiency of solar cells.

Fig 5 displays the EDX spectrum for the above said CuS_{Se} thin film. In this spectrum, the Cu peak was found at 1keV, S at 2.5keV, Se at 1.5keV and weight ratios of these elements are 11.66%, 4.06% and 84.28% respectively.

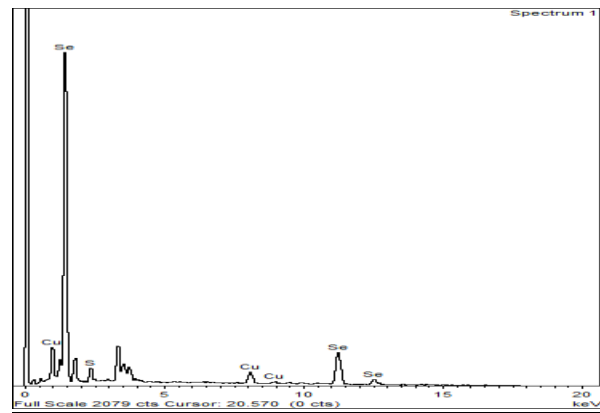


Fig.5. EDX spectra of CuS_{Se} thin film

3.3 Optical properties

The optical properties of the deposited thin films were investigated using UV-1800 in the wavelength range between 300-1100nm. These measurements include absorption, transmittance and reflectance. Optical constants such as band gap values (E_g), extinction coefficient (k), and absorption co-efficient (α) are calculated using transmittance spectral data.

3.3.1 Optical Absorption, Transmission and reflectance spectra

The absorption spectra of deposited CuS and CuS_{Se} films are as shown in Fig.6. The “absorbance” (i.e. photometric value) is a measure of the amount of light absorbed by the sample under specified conditions. An absorption edge corresponds to an electron excited by a photon of known energy, whereby electron can jump from a lower energy to a higher energy state. The absorption spectrum of CuS thin films was recorded in the above said wave length region and the absorption edge is between 450nm and 550nm. It was observed that after the selenization absorption edge is shifted towards longer (blue shift) wave length side between 880nm and 930nm, arising from quantum

confinement effect in nano crystalline film, which suggests a decrease in the band gap value.

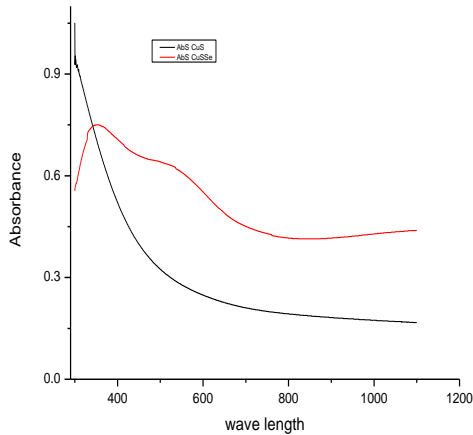


Fig.6. Absorption spectra of CuS and CuSSe thin films

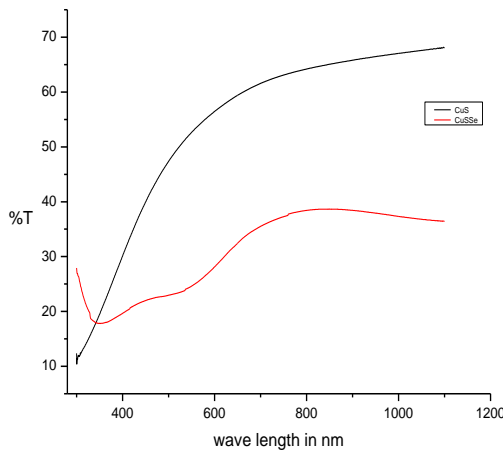


Fig.7. Transmittance spectra of CuS and CuSSe thin films

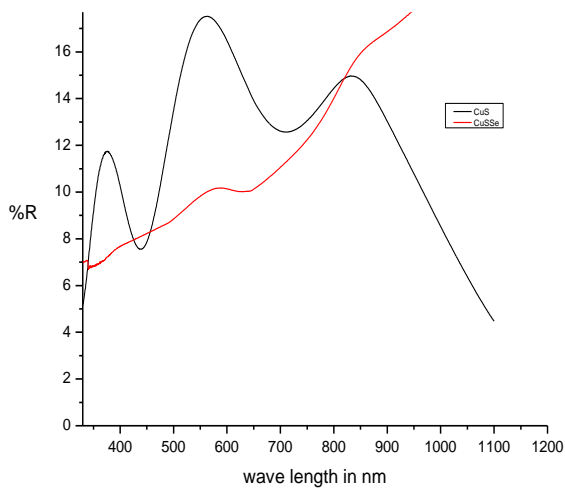


Fig.8. Reflectance spectra of CuS and CuSSe thin films

Transmission spectra of thin films cf. Fig.7 shows interference pattern with moderate sharp fall of transmittance at the band edge, which is an indication of

good crystalline structure [23]. The CuS thin film shows the transmittance up to 70%, after selenization it is reduced to 40%. This intern increases the absorption. After selenization, maximum absorption is observed in the visible region, and slightly in the NIR region. Due to this, increase in the efficiency of the solar cell is expected.

The variation of reflectance (R) with wavelength for CuS and CuSSe thin films is as depicted in Fig.8. For CuS thin film reflectance is more at visible region but after selenization reflectance decreases, intern helps to absorb more light in this region. So, efficiency is expected to increase.

3.3.2 Absorption and extension coefficient

Absorption coefficient (α), optical band gap (E_g), and extinction coefficient (k) are the optical constants of a material are determined from its optical behaviour of thin film. The absorption coefficient (α) has been obtained directly from the absorbance against wavelength using the following relation [24],

$$\alpha = \text{Absorbance}/\text{thickness} \quad (2)$$

The variation of the absorption coefficient (α) as a function of incident photon energy ($h\nu$) for CuS and CuSSe thin films are as depicted in Fig.9. It has been observed that the absorption coefficient (α) increases with the increase in photon energy for CuS and CuSSe thin films. In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge.

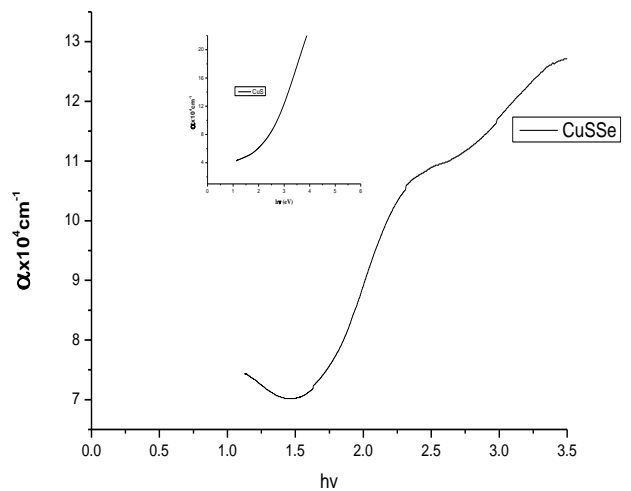


Fig.9. Variation of Absorption co-efficient (α) with photon energy for CuSSe (Inset corresponds to CuS thin film)

α is also related with the extinction coefficient (k) by the following relation [25]

$$k = \alpha\lambda/4\pi \quad (3)$$

The dependence of k on the photon energy obtained from Eq. (3) for CuS and CuSse thin films are as shown in Fig.10.

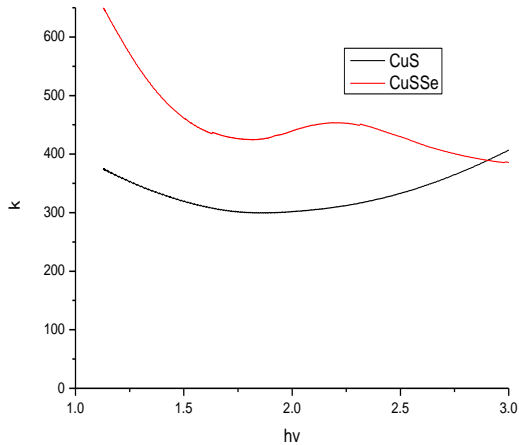


Fig.10. Variation of extinction coefficient (k) with photon energy for CuS and CuSse thin films

3.3.3 Band gap

The optical absorbance is a powerful method to determine the energy gap. It is well known that α is related to the photon energy which is used to measure the optical band gap (E_g) and to determine the nature of the optical transitions. The optical band gap can be found in the high absorption and is characterized by the following expression [25, 26]

$$(\alpha hv) = C_a (hv - E_g)^n \quad (4)$$

Where C_a is the constant, ν is the frequency, E_g is the optical band gap, h is the Planck's constant, and n is a number which relates the mechanism of the transmission process, where $n = 1/2$ for direct transition, $n = 3/2$ for directly forbidden transition, $n = 2$ for indirect transition and $n = 3$ for indirectly forbidden transition. In amorphous thin films the band gap was obtained with $n = 1/2$ means a directly allowed transition between the valence and the conduction band. The linear nature of the graphs supports the direct band gap nature of the semiconductor. It is well known that direct transitions across the band gaps are feasible between the valence and the conduction band edges in the k -space (wave number). In this process, the total energy and momentum of the electron-photon system is conserved [25].

Variation of $(\alpha hv)^2$ with photon energy (hv) for CuS and CuSse thin films are reported in Fig.11. The value of the band gap was evaluated at $\alpha=0$. The observed values of E_g are given in Table-2. The decrease in the band gap value after selenization intern may increase the efficiency of solar cells.

Table.1 optical parameters of CuS thin film before and after selenization

Sl.No	Thin films	Band gap in eV
1	CuS	2.05
2	CuS after selenization (CuSse)	1.60

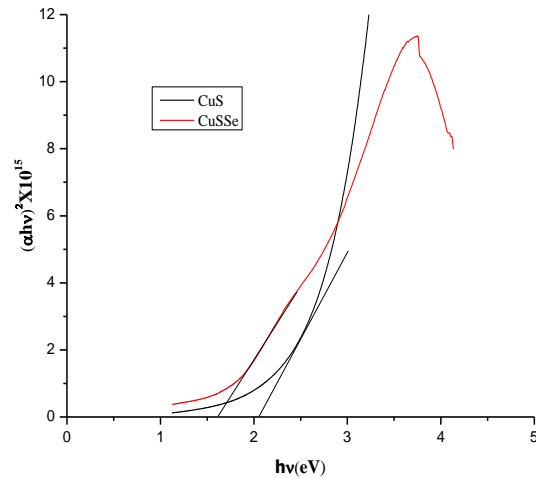


Fig.11. Variation of $(\alpha hv)^2$ with photon energy (hv) for CuS thin film before and after selenization.

Conclusion

In summary, we have fabricated a novel, high quality and low cost CuSse thin film by using simple non vacuum techniques, which is hitherto not known. The structural, surface and optical properties of the fabricated thin film were investigated. Structural characterization proves the formation of CuSse phase and particles are in nano crystalline state. The EDX spectrum reveals the presence of elements like Cu, S and Se and its percentage weight ratio. The optical study of the prepared film shows good absorption in the NIR region and also reveals the decrease in band-gap with the incorporation of selenium. Surface analysis shows that particles are crystalline in nature and closely packed. Fabricated CuSse thin film is a very good absorbing layer for solar cells, based on the capability of the Group-II ions to inhibit the movement of the copper ions towards the n-side of the photovoltaic junction. Further, this thin film has low transmittance and high reflectance in the IR region, and moderate transmittance and low reflectance in the visible region. The above optical property of the fabricated thin film is ideal for solar control applications.

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